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Parabenzoyldiphenylsulphone
and
Related Compounds.

Dissertation
submitted to the Board of University Studies
of Johns Hopkins University for the degree
of Doctor of Philosophy
by

Lyman C. Newell.

1895.

71.249

Contents.

I. [illegible] 1

II. [illegible] 3

III. [illegible]

[illegible] 3

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IV. [illegible]

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[illegible] 7

[illegible] 8

[illegible]

[illegible] 9

[illegible] 10

[illegible] 11

V. [illegible]

[illegible] 12

[illegible] 14

[illegible] 15

VI.

VII.

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IX.

1. —

benzophenonesulphone, $C_6H_4 < \begin{matrix} CO.C_6H_5 \\ SO_2.C_6H_5 \end{matrix}$ (1) (3). This compound was obtained by Saunders[1] in 1874 by the action of benzene and aluminium chloride on benzenesulphobenzoic acid. The general plan was to start with toluenesulphochloride, $C_6H_4 < \begin{matrix} CH_3 \\ SO_2Cl \end{matrix}$ (1) (2), to couple it with benzene by the aid of aluminium chloride, thus obtaining tolylphenylsulphone, $C_6H_4 < \begin{matrix} CH_3 \\ SO_2.C_6H_5 \end{matrix}$; to oxidize this

[1] Journ. Chem. Soc. 17, 362.

It was deemed advisable to begin the work in the para series, and as the results have been so fruitful, nearly the whole investigation has been confined to this series.

II. Chloride of Picolinol.

The starting point of this investigation was [illegible]. The second substance used was prepared by the usual method and was a kilogram of the chloride which had been [illegible] in the preparation of the ortho analogue. The raw product was washed with cold water, sucked hard on the filter pump to remove [illegible] and recrystallized from ordinary ether.

III.

and Blair[1] in 1878 from benzenesulphonic acid,

and aluminium chloride or benzenesulphone-

chloride; and by K. Otto[2] in 1885 from benzene-

sulphonecarbide, benzene and mercury chloride;

the product obtained by these different methods

melted at 124°–125°, and was either

[1] Ber. 11, 116. [2] Ber. 11, 1063. [3] Ib. 18, 2

[illegible]

0.2000 gram of the [illegible] gave [illegible]

[illegible] 0.0041 gram H_2O.

Calculated for [illegible]

$(C_6H_4{<}^{CO}_{SO_2}{>}C_6H_5)_2Ca + \frac{1}{2}H_2O$

H_2O	1.5%	1.7%

0.2205 gram [illegible] gave 0.0561 gram $CaSO_4$.

$(C_6H_4{<}^{CO}_{SO_2}{>}C_6H_5)_2Ca$

Ca	7.11	7.15

0.2[illegible] grams [illegible] dried [illegible] 110°

to constant weight [illegible] 0.[illegible] = 1.0.

Calculated for [illegible]

$(C_6H_4{-}SO_2{-}C_6H_5)_2Cu + 5H_2O$

H-O [illegible] [illegible]

0.2[illegible] grams [illegible] anhydrous salt gave [illegible] 0.0[illegible]4 grams $CuSO_4$.

Calculated for [illegible]

$(C_6H_4{-}SO_2{-}C_6H_5)_2Cu$

Cu 10.81 10.5[illegible]

	Berechnet für	Gefunden
H_2O	11.41	10.5–

0.1603 gramm desinfektionsalz verlor gramm 0.0414 gramm H_2O.

	Berechnet für $C_6H_4 \begin{matrix} COONa \\ SO_2C_6H_5 \end{matrix}$	Gefunden
Na	8.11	7.93.

V. Paraäthoxylaminphenolbenzoyläther.

Paraäthoxylaminphenol wurde in 5 Teilen
wasserfreiem Pyridin gelöst. Zu
dieser Lösung wurde Benzoylchlorid

0.1697 gram chloride gave 0.0845 gram AgCl.

	Calculated for $C_{13}H_9SO_3Cl$	Found
Cl	12.62	12.31

the results were:

Cl 12.6 c. 12.4 c.

[illegible] 137°, it lost 0.0043 gram. In the analysis, general conduct, and method of formation, this chloride has been given the formula

$C_6H_4 < \overset{COCl}{SO_2C_6H_5}$.

[illegible]

[illegible]

[illegible]

[illegible]

compound to be the amide corresponding to benzenesulphonyl chloride, and we accordingly it has been given the following formula

$$C_6H_4 \begin{cases} CO.NH_2 \\ SO_2.C_6H_5 \end{cases}.$$

XII. [illegible]

I. 0.2944 gram gave 10.4 c.c. - 401.18 mm. ... to gram under standard conditions.

II. 0.3073 gram gave 0.213 gram $BaSO_4$

	Calculated for $C_{16}H_{17}O_3NS_2$	Found I.	Found II.
N	4.16	4.00	...
S	9.48	...	9.52

... of benzenesulphonyl ... with ... of phosphorus pentachloride ...

$C_6H_4 \begin{cases} CO.NHC_6H_5 \\ SO_2.C_6H_5 \end{cases}$.

VIII. ...

... para-toluenesulphonchloride into benzoylphenylsulphone (see p. 14), was melted on the ... of ...

I. 1.15 of grain gave 0.385 gram CO_2 and 0.165 gram H_2O.

II. 0.1515 " " 0.0508 "

III. 0.1515 " " 0.0508 "

IV. 0.2 " " 0.085

	$C_{19}H_{14}O_3$	I.	II.	III.	IV.
C.			..	...	..
H	4.65	4.70	.	..	4.8
O	7.75	...	7.57	7.53	7....

The determinations of carbon and hydrogen were made by the Dennis modification of the lead chromate method; the first two determinations of sulphur were made by [illegible] of Ames.

[illegible]

[illegible]

IX.

$$C_2H_4 \begin{matrix} SO_2C_2H_5 \\ -SO_2C_2H_5 \end{matrix}.$$

I. 0.1980 grm. Sub. = 0.1852 grm. H_2O, and 0.4852 grm. CO_2

II. 0.1978 " " 0.4857 " CO_2 " 0.0801 " H.

III. 0.1005 " " 0.1104 " $BaSO_4$.

IV. 0.1625 " " 8.12 C.C. = 0.0103 grm. nitrogen,

same condition as in the analysis of

(see p. 30).

$C_6H_5.SO_2.C_6H_4.C.C_6H_5$
‖
N.NH

or

HO.N

X. C

The results of this investigation may be briefly summarized as follows:

1. Phenol-4-sulphonic chloride by means of the

2. This sulphone can be best oxidized by chromic acid to p-sulphobenzoic acid, which forms well characterized salts.

3. When treated to 140° with fuming sulphuric acid, it changes to the disulphonic acid, which forms

$C_6H_5.SO_2.C_6H_4.C.C_6H_5$ or $C_6H_5.SO_2.C_6H_4.C.C_6H_5$.
‖ ‖
N.·H HO.N